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Order parameter from birefringence studies of two mesogens : 4-propyl paraethoxy phenyl cyclohexyl carboxylate and 4-butyl paraethoxy phenyl cyclohexyl carboxylate

Saswati Chakraborty, Anuradha Mukhopadhyay* and S K Roy[1]
Department of Physics, Jadavpur University, Kolkata-700 032, India
[1]Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700 032, India

E-mail : anuradha_mukhopadhyay@yahoo.com

Abstract : Texture and optical studies as a function of temperature have been conducted on two mesogenic members : code names D302 and D402 of the alkyl phenyl cyclohexyl carboxylates series to study the effect of increasing chain length. The transition temperatures of the two members were confirmed from texture studies. From birefringence studies, the refractive indices n_e and n_o were determined and density measurements were made to obtain the orientational order parameter at various temperatures. The effect of increasing chain length of the molecules on the optical properties and thereupon on the OOP has been discussed. Comparison of experimentally obtained values has been made with the theoretical values obtained from Maier-Saupe theory.

Keywords : Thermotropic, mesogens, birefringence, polarisability, order parameter.

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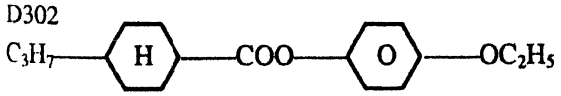
1. Introduction

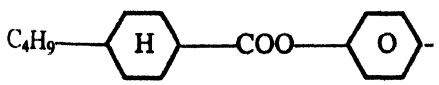
The mesogen 4-propyl paraethoxy phenyl cyclohexyl carboxylate (code name D302) and 4-butyl paraethoxy phenyl cyclohexyl carboxylate (code name D402) are the members of the homologous series alkyl phenyl cyclohexyl carboxylates having the chemical and structural formulae as given below :

D302



Molecular formula : $C_{19}H_{26}O_3$

D402



Molecular formula : $C_{19}H_{28}O_3$

NMR [1,2] and optical studies [3] have been conducted on the above compounds. NMR studies [2] have revealed the formation of a new phase (either a plastic or a cubic phase) on cooling for each of the mesogens. Optical studies (λ unspecified) using standard procedure *i.e.* Abbe's refractometer have also been reported [3]. In the present work, texture and optical studies have been conducted on the mesogenic samples at various temperatures. The optical studies have been performed by the application of the Chatelain-Wedge principle using a He-Ne laser (λ = 633 nm) as the light source. The highly intense He-Ne laser beam allows the readings to be taken on a screen held at a large distance from the sample material, thereby affording much greater accuracy. The polarisability and orientational order parameter of the compounds have been determined therefrom and a comparative study of the two compounds have been made to study the effect of increasing chain length.

The compounds are known to undergo the following phase transitions [Merck Ltd]

D302

	48°C		78°C	
Solid		Nematic		Isotropic

*Corresponding Author

D402

	37°C		75°C	
Solid	→	Nematic		Isotropic

2. Experimental methods

(A) Texture studies :

The transition temperatures were noted using a polarizing microscope (Leitz) in conjunction with a hot stage (Mettler FP 82 HT). Observations were made under crossed polarizers with a magnification of 150X. Heating and cooling were done at the rate of 1°C/min. Both the samples were heated to temperatures well above the isotropic transition temperatures and then allowed to cool. Texture photographs were taken of the sample in the nematic phase.

(B) Optical studies :

Birefringence studies were conducted on the sample in the presence of an ordering magnetic field. The refractive indices n_e and n_o of the extra – ordinary and the ordinary rays were measured at different temperatures from which the polarisibilities α_e and α_o could be calculated using density measurement.

Prisms with angle of the order of 1°–2° were constructed using glass slides whose inner faces were treated with polyvinyl alcohol and rubbed for better alignment of the sample. The liquid crystal sample was then introduced by melting the sample at the top of the open edge and allowing the melted sample to flow in. The open edge was then sealed. The sample holder (built in-house) with the prism is placed within the pole pieces of an electromagnet in a manner such that the direction of rubbing (along the prism edge) is along the magnetic field. Magnetic field strength of ~8 KGauss was used. The combination of rubbing and magnetic field along the same direction produces a homogeneous monodomain specimen, the optic axis being parallel to the edge of the prism. Light from a He-Ne laser (λ = 633 nm) was directed normally on the sample through a hole drilled in the sample holder. The angular deflections of the refracted beams were measured by observing the light spots on a screen held ~6 meters away. From the changes in the patterns observed on the screen the transition temperatures may be verified. They were found to be in conformity with the temperatures found from texture studies. The samples were heated at the rate of 1°C/min to temperatures beyond the isotropic temperatures and allowed to cool at the same average rate. From angular deflection measurements the refractive indices n_e and n_o were calculated over the nematic range. The spot separation varies but is typically of the order of 1 cm. The spot has a finite dimension and measurements are taken of both the top and bottom ends of each of the circular spots and mean of these used for calculation. The details of the experimental arrangement have been discussed in Ref [4].

To obtain the polarisibilities α_e and α_o necessary for calculation of order parameter, the density of the compounds were determined as a function of temperature. This was done by putting the weighted samples in a glass capillary tube, which was then placed in a heat bath. The length of the column was measured with a traveling microscope at various temperatures and thereby densities determined as a function of temperature.

3. Results and discussion

(A) Texture studies :

The transition temperatures observed are in excellent agreement with the quoted values supplied by Merck and are given below :

D302

	48°C		78°C	
Solid	→	Nematic	→	Isotropic
			←	
			77°C	

D302

	37°C		75°C	
Solid	→	Nematic	→	Isotropic

However, on cooling no change in texture was observed up to 30°C for both the samples (further lowering of temperature not being possible for experimental shortcoming) indicating the presence of a supercooled nematic phase.

The texture photographs of D302 and D402 confirming the nematic phase have been shown in Figures 1 and 2.

(B) Optical studies :

From birefringence studies n_e and n_o were obtained at different temperatures throughout the nematic range. The variations of refractive indices with temperature are depicted in Figure 3. From birefringence studies and density measurements, the molecular polarisabilities (α_e,

α_o) have been calculated using Vuks' formula [5]. The order parameter $\langle P_2 \rangle$ were calculated using the relation

Figure 1. D302, Nematic phase at 70°C (cooling)

Figure 2. D402, Nematic phase at 40°C (heating).

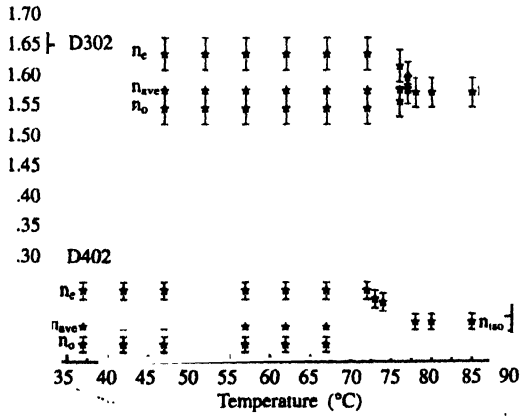


Figure 3. Variation of refractive index with temperature.

$\langle P_2 \rangle = (\alpha_e - \alpha_o)/(\alpha_{\parallel} - \alpha_{\perp})$ [6] where α_o and $\alpha_{\perp}$ are the polarisabilities parallel and perpendicular to the long axis and have been obtained using extrapolation procedure of Haller *et al* [7]. The theoretical values of order parameter were calculated using Maier-Saupe theory [8]. The estimated corresponding errors have been depicted on the diagram.

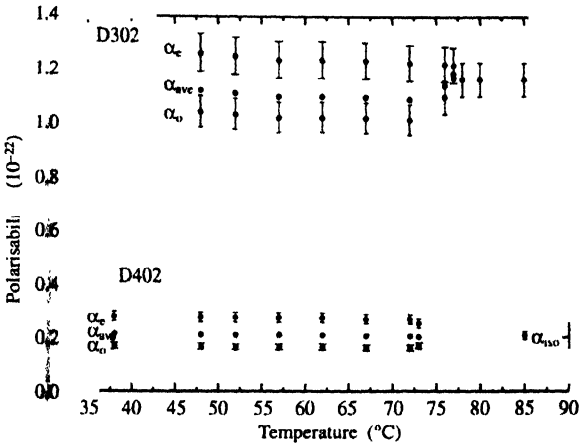


Figure 4. Variation of polarisability with temperature.

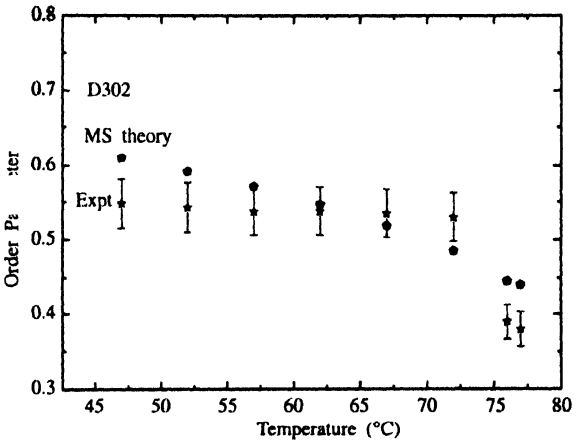


Figure 5. Variation of order parameter with temperature.

From Figure 3 it is evident that there is no perceptible variation of refractive indices with temperature for both D302 and D402. The quoted value (as supplied by Merck) of the optical anisotropy Δn is 0.09 for both the compounds and agrees exactly with the experimental values obtained. No discontinuity is exhibited in the values of n_{ave} and n_{iso} at nematic-isotropic transition temperature for D402 whereas a perceptible difference between n_{ave} and n_{iso} is observed for D302. It has been suggested in Ref. [3] that this discrepancy in n_{ave} and n_{iso} is exhibited by molecules of high molecular dipole moments of the order of 4–5 Debye whereas molecules of smaller dipole moments of the order of 2 Debye do not exhibit a discontinuity. At this juncture, we are not in a position to comment on the authenticity of this observation since work on molecular dipole moment

calculation is still in progress. However the value of refractive indices of D402 is significantly lower than that of D302.

The polarisability curve of D302 and D402 are distinctly different whereas for D402, polarisabilities are nearly temperature independent average polarisability for D302 increases markedly as the isotropic temperature is approached indicating a significant change in the density of the same near isotropic transition. The polarisability anisotropy for D302 is much greater than D402 and remais fairly constant at ~0.22 whereas that for D402 varies from 0.11 to 0.06 in the nematic range.

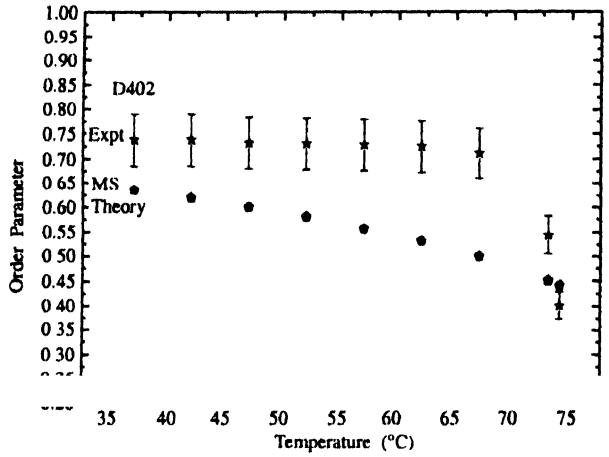


Figure 6. Variation of order parameter with temperature.

The experimental order parameter values for both the samples prior to NI transition (0.38 for D302 and 0.40 for D402) are very close to the predicted Maier Saupe value of 0.429, though the nature of variation in the nematic region disagrees with the gradual decrease of $\langle P_2 \rangle_{ms}$ suggesting deviation from the mean field theory. However in general $\langle P_2 \rangle$ is higher for D402 (0.73–0.4) than for D302 (0.55–0.38) indicating a greater ordering with increased chain length.

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